



# Solar-assisted bacterial disinfection and removal of contaminants of emerging concern by $\text{Fe}^{2+}$ -activated $\text{HSO}_5^-$ vs. $\text{S}_2\text{O}_8^{2-}$ in drinking water

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## ARTICLE INFO

### Keywords:

Solar disinfection (SODIS)  
*Escherichia coli*  
Micropollutants  
Drinking water treatment  
Peroxydisulfate (PDS)  
Peroxymonosulfate (PMS)

## ABSTRACT

This research demonstrates the feasibility to enhance solar disinfection (SODIS) treatment by addition of peroxymonosulfate (PMS) and peroxydisulfate (PDS) by the generation of sulfate (and hydroxyl) radicals through different activation routes. The different promoters were i) sunlight irradiation, ii) mild heat (40 °C), and iii)  $\mu\text{M}$  amounts of  $\text{Fe}^{2+}$ , all present during actual field SODIS experiments, or voluntarily added alongside PMS/PDS. In a first approach, the promoters were studied separately, in pairs and finally all together in a combined process (CP). In all the cases, PMS showed a higher efficiency than PDS in *E. coli* removal, requiring lower concentration and a faster reaction time towards total bacterial inactivation. Therefore, the combined process (Oxidant/ $\text{Fe}^{2+}$ /Sunlight/40 °C) reached total bacterial inactivation (6-logU) in 30 min when PMS was used, while it took twice as long with the PDS. These effects can be further enhanced when PMS with  $\text{H}_2\text{O}_2$  is used, and barely 20 min are needed for complete bacterial removal. Besides total disinfection, the combined processes were suitable to eliminate micropollutants in  $\mu\text{g/L}$  concentration (drugs, pesticides, etc.) during solar treatment. Finally, the efficiency of the treatment methods was successfully tested in a lake water matrix, in a feasibility assay as a potential drinking water treatment method. The economic analysis highly supports the use of these oxidants. Although the use of PMS or PDS increases the cost of treatment, it is not mandatory to add other reagents or external activators; iron is ubiquitous in natural water and can act as activator, while during SODIS sunlight irradiation can provide UV and mild water heating, hence act as an effective disinfection method. Finally, a mechanistic proposal for the combined processes is given, as an overview of the occurring reactions leading to bacterial inactivation.

## 1. Introduction

According to the World Health Organization [1], in 2015 approximately 2 billion people were supplied drinking water from fecal-contaminated sources. The presence of pathogens is responsible for waterborne illness, hindering human development, decreasing life expectancy and inflicting other side-effects to the affected populations, such as economic losses due to inability to work [2]. As such, the United Nations established the 6<sup>th</sup> Sustainable Development Goal to ensure availability and sustainable management of water and sanitation for all. One of the developed measures is the point-of-use solutions for

developing countries; these implementations should be easy to use, safe, cheap and environmentally sustainable [3].

Among the approved interventions we encounter solar disinfection of water (SODIS). Sunlight has been widely reported as an efficient, cheap and environmentally-friendly to inactivate microorganisms in natural surface waters and drinking water [4–7]. Although this process has documented efficiency and practical simplicity, there are issues related with the temperature dependence of the disinfection efficiency and the risk of bacterial regrowth after treatment [8,9]. A solution might be given by solar-driven Advanced Oxidation Processes (AOPs), which enhance the efficiency of SODIS through the generation of highly

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<https://doi.org/10.1016/j.apcatb.2019.02.018>

Received 26 November 2018; Received in revised form 27 January 2019; Accepted 9 February 2019

Available online 11 February 2019

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oxidative species, in a rather flexible range of SODIS container volumes, and a simple configuration under simple solar light exposition [10–14]. For instance, the use of certain substances at low concentration, such as hydrogen peroxide [15,16], peroxydisulfate (PDS) [17] and peroxymonosulfate (PMS) [18], anions and/or iron [19,20], which in some cases can be naturally present in water, have been successfully reported to inactivate potentially pathogenic species such as bacteria, viruses and yeasts [21–23], as well as degrading harmful organic contaminants [24–26]. These harmful substances, also known as micropollutants, are usually detected at trace levels in water bodies and are of growing concern for water quality. For this reason, it is important to find treatment methods able to disinfect and to remove micropollutants at the same time [25,27,28].

Sulfate radical-based AOPs are gaining increasing attention over the last years [29–31] because of their high redox potential (2.6 eV) and long life-time of the generated radicals. Sulfate radicals are generated from either PDS or PMS, both oxidants acting as initiators. Even if PDS and PMS are strong oxidizers, with the redox potential of 2.01 V and 1.82 V respectively, they do not have high bactericidal capacity by themselves and need to be activated via one of the following methods: i) heat [32]; UV radiation [33,34]; alkaline conditions [35] or transition metals [36–38]. Nevertheless, literature lacks information for their activation in mild conditions that would enable their use in drinking water treatment (safe for human consumption) or in the most economical use. The key lies in their use in low  $\mu\text{M}$  amounts, as their application in the cheap SODIS would require; only recently the capacity of PDS to play this role was assessed [39].

Furthermore, to the best of the authors' knowledge, there are no works about the comparison of PDS and PMS towards the enhancement of solar disinfection. In fact, the number of works reporting the use of both oxidants for disinfection or removal of micropollutants is scarce [25]. Most commonly, both oxidants have been separately studied to remove organic pollutants [32–34,37]. In addition, the disinfection efficiency of persulfate has traditionally been compared with hydrogen peroxide [17,40–42], while there are very few references about the efficiency of PMS as disinfectant [18,43,44]. This is the first time that their feasibility is challenged, and hereby suggested as a low cost technology to treat drinking water in developing countries.

In this work, we induce a solar-assisted photo-catalytic cycle of sulfate radical generation, towards the disinfection (bacteria) and decontamination of water (micropollutants). More specifically, solar water disinfection (SODIS) enhancement using sulfate radicals is evaluated through persulfate (i.e. PMS and PDS, respectively) activation using three activation factors, namely solar light, iron and heat. *E. coli* inactivation is systematically monitored in a comparative way between PMS and PDS, in order to assess their effectiveness, and micropollutant degradation in the optimal conditions is tested complementarily. For comparison with a well-studied process, benchmarking of the two processes is performed with the solar photo-Fenton system. The disinfection mechanisms and the differences in the inactivation of bacteria are interpreted, providing insight on the induced photo-catalytic cycle. Finally, the capability of these processes to disinfect actual drinking water was assessed, and an integrated proposition for mechanistic interpretation of bacterial disinfection was finally proposed.

## 2. Material and methods

### 2.1. Chemical and reagents

Chemicals and reagents were used as received. potassium peroxymonosulfate ( $\text{KHSO}_5$ ; Sigma-Aldrich; PMS), sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ; Sigma-Aldrich; PDS) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ; Sigma-Aldrich) were used as oxidant in different concentrations. Iron (II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; Sigma-Aldrich) was used as activator of PMS and PDS. Finally, tert-butanol (TBA,  $\text{C}_4\text{H}_{10}\text{O}$ , Sigma-Aldrich) was used as scavenger to determine the nature of the formed

radicals. MilliQ water (Millipore Elix Advantage 3, Millipore AG) was used for aqueous solutions' preparation (15.8 M $\Omega$  cm).

### 2.2. Experimental setup

In order to assess the bacterial inactivation through the different processes, cylindrical double-wall Pyrex glass reactors were used, with 9 cm height, 7.5 outer diameter and 6.5 cm inner diameter. Before each experiment, sterilizing of materials and reactors took place by autoclaving (121 °C). The reactors have a double-wall allowing recirculation of water and control of reaction temperature. The temperature control was performed by water and attained by thermostat (F25 Refrigerated/Heating Circulator, JULABO GmbH). The double-wall trait of the reactors makes the circumference impenetrable to light, so solar UV was provided only from the top of the reactors. A thin, borosilicate glass cover was placed on top of the reactors, to filter out the emitted UVB wavelengths, similarly to the real conditions of SODIS by PET or glass bottles whose transmittances does as such (see Supplementary Figure S1, cut-off at  $\sim 310$  nm). A magnetic bar was introduced for mixing, and the reactors were placed on a magnetic stirrer; all reactions were carried out under agitation ( $\sim 350$  rpm). After every experiment, reactors were soaked overnight in nitric acid, and washed multiple times with ethanol to remove organic traces and demineralized water in abundance.

Light was provided to the system by a bench-scale solar simulator (SUNTEST CPS, Hereaus), which bears a 1500-W Xenon lamp. The system was air-cooled, and provided with IR and UV-C cut-off filters. The irradiance used in the experiments (900 W/m<sup>2</sup>) was measured by a pyranometer (CM6b, Kipp & Zonen).

The lake water tests were performed bearing in mind the field application. For this purpose, 500-mL PET Coca-Cola™ bottles were used, after washing with warm water. Four bottles were placed into a recipient (acting as a water bath) adjusted to the illumination surface of the solar simulator, and the water temperature was again controlled by a thermostat. Water covered 20–30% of the circumference and the rest was exposed to direct solar irradiation. No stirring took place, similarly to the actual SODIS conditions. Before sampling, gentle shaking took place to “homogenize” the water and acquire a “representative” sample for bacterial enumeration.

### 2.3. Analytical methods

#### 2.3.1. *Escherichia coli* K12 preparation and enumeration protocols

The bacterial inactivation experiments were carried out using a wild type *Escherichia coli* strain K12, acquired from Deutsche Sammlung von Mikroorganismen und Zellkulturen (DSMZ, No. 498) as bacterial model. This specific strain variant is non-pathogenic and allows a good approximation of naturally occurring *E. coli*, which is a well-known indicator bacterium for enteric pathogens. The preparation of the bacterial stock took place as previously published [39,45]. Briefly, growth of the strain to stationary phase was attained by creating overnight aerobic cultures in spiked LB medium at 37 °C, followed by 3 times washing by a sterile saline solution (8 g NaCl/0.8 g KCl in 1 L water). The final pellet was re-suspended in saline solution and enumerated (around 10<sup>9</sup> CFU/mL).

In order to quantify the bacterial concentration, timely acquisition of 1-mL samples was performed, and via proper aliquots and the standard plate count method on plate count agar (PCA) the bacterial concentrations were measured. Colony forming units (CFU/mL) were counted after 24 h incubation in the dark at 37 °C. Hereon, the 6-log reduction in cultivable bacteria will be mentioned as total inactivation, with the bacterial cultivability being the proxy for bacterial activity.

#### 2.3.2. Micropollutants' determination

The micropollutants' concentration was determined by an online SPE-UPLC®/MS-MS (Acquity Xevo-TQ, Waters) method, previously

published [39,46]. After HCl-mediated acidification of the samples at pH = 2, a standard mixture of the surrogate contaminants was spiked in their deuterated form. After filtration, samples were injected in an SPE column (Oasis HLB 25 µm, 2.1 × 20 mm, Waters) with acidified ultrapure water as eluent (1% formic acid). An Acquity HSS T3, 1.8 µm, 2.1 × 100 mm Waters column was used, and a gradient of ultrapure water and acetonitrile was used, after acidification at 0.1% with formic acid. The detection of micropollutants was done by multiple reaction monitoring and their exact quantification was achieved with internal standard calibration. The estimation of abatement was made by calculating the percentage removal of mol for each species and combining them in a weighted average for each sampling point of each experimental condition [39,46].

### 3. Results and discussion

#### 3.1. Control experiments (no activation of PMS and PDS)

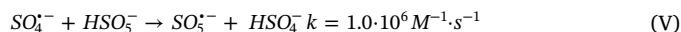
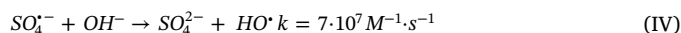
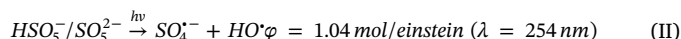
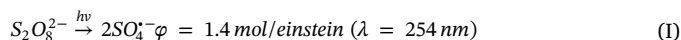
The disinfection efficiency of PDS and PMS was tested at different concentrations ( $1.8\text{--}9.0 \cdot 10^{-5}$  M) (Figure S2, Supplementary Material), in the dark and at 20 °C temperature. While the cultivable bacterial concentration remains stable within the 5 h of reaction with PDS at  $9.0 \cdot 10^{-5}$  M, total inactivation was reached after 4 h using the same concentration of PMS. In the studied conditions, PMS is able to inactivate *E. coli* by itself, while PDS will require the use of any activators. The reduction of *E. coli* population is consequence of the PMS and bacterial membrane redox potential of 2.01 V [29] and 0.7 V [47,48] respectively. For that, the reaction among membrane and oxidant is slow but thermodynamically possible. Most probably, the same pathway with PDS is not clearly manifesting bacterial inactivation, due to slow reaction kinetics that are controlled by the concentration added.

#### 3.2. PMS and PDS single factor activation: evaluation of activation methods

Because of the lack of disinfection effect of PDS by itself at the employed concentrations, and the requirement of a high reaction time (4 h) to show disinfection activity of PMS, the use of activator agents is required. Different activation factors such as solar light radiation, heat and  $\text{Fe}^{2+}$  were assessed individually.

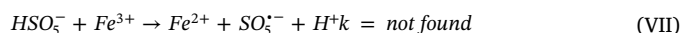
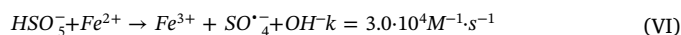
Fig. 1A shows the bacterial inactivation under simulated solar light, varying the concentration of PMS and PDS. As observed, the addition of  $1.8 \cdot 10^{-5}$  to  $9.0 \cdot 10^{-5}$  M of PMS significantly improved the inactivation rates, compared to SODIS and PDS/SODIS. After 300 min, SODIS alone reached an *E. coli* inactivation of 2.88 logU, while total inactivation was reached in less than 150 min using  $1.8 \cdot 10^{-5}$  M of PMS, where disinfection was incomplete and slow. The increase of oxidant concentration led to reduced solar exposure time for the two reactants in an apparent linear way. Meanwhile, Fig. 1B shows thermal activation of PMS and PDS at 40 °C. Previous assays showed that at 50 °C thermal-driven bacterial inactivation occurs [39]. However, the latter effect is not observed at 40 °C (Fig. 1B). Thermal activation of PMS exhibits total inactivation with all concentrations in less than 30 min (i.e. 15 min with  $9.0 \cdot 10^{-5}$  M). In contrast, with PDS, bacterial decay starts only after 180 min of treatment, reaching a maximum removal of 3 logU after 300 min, with the highest PDS concentration. Finally, Fig. 1C shows the tremendous difference that PDS and PMS activation by 1 mg/L ( $1.8 \cdot 10^{-5}$  M) of  $\text{Fe}^{2+}$  has in the dark, at 20 °C, varying the oxidant's concentration. The highest efficiency was reached with PMS/ $\text{Fe}^{2+}$  ratios of 1:2 and 1:5, while  $\text{Fe}^{2+}$  alone has a limited capacity of PDS activation.

Concerning the mechanism of inactivation, under light exposure, the above mentioned results agree with a possible differentiated quantum yield of both oxidants under UV–C [49]. Although the generation of sulfate radicals occurs by fission of O–O bond of PDS and PMS by higher energy wavelengths (Eqs. I and II); a proportionality could exist in the emitted UVA wavelengths used in this research.

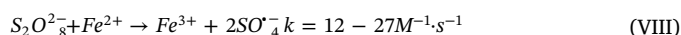


Another important factor to consider is the generation of hydroxyl radicals, with 10 times higher reactivity with biomolecules, compared to sulfate radicals [44], in the activation of PMS (Eq. III). This effect could explain the larger efficiency of PMS. These hydroxyl radicals are mainly formed within the PDS cascade of reactions as a consequence of  $\text{SO}_4^{\cdot-}$  reaction with water, or neutralization with  $\text{OH}^-$  (Eqs. III–IV). Besides this process, sulfate radicals react with PMS in the medium, generating sulfur pentoxide radicals  $\text{SO}_5^{\cdot-}$  (Eq. V). The generated sulfur pentoxide radical has a lower redox potential than hydroxyl and sulfate radicals ( $E^\circ = 1.1$  V), but thermodynamically speaking it could oxidize the bacterial cell wall itself. On the other hand, the thermal activation of PMS and PDS follows the same pathways as UV-based activation described above (Eqs. I and II). It was previously reported [50] that hydroxyl radicals are the main radicals during the heat activation of PMS. Our results corroborate that in single-factor activation the main difference, apart from the baseline PMS inactivation might be the generation of  $\text{HO}^{\cdot}$ .

In the iron mediated activation, two main reactions occur when coupling PMS/ $\text{Fe}(\text{II})$  (Eqs. VI and VII). It is suggested that  $\text{Fe}(\text{II})$  acts as electron donor, provoking the rupture of peroxo-bond in the PMS structure (Eq. VI). In parallel, the  $\text{Fe}^{3+}$  formed from the previous oxidation reaction acts as an electron acceptor, further activating the PMS (Eq. VII).



However, in the case of PDS (Eqs. VIII),  $\text{Fe}^{3+}$  does not react with PDS.

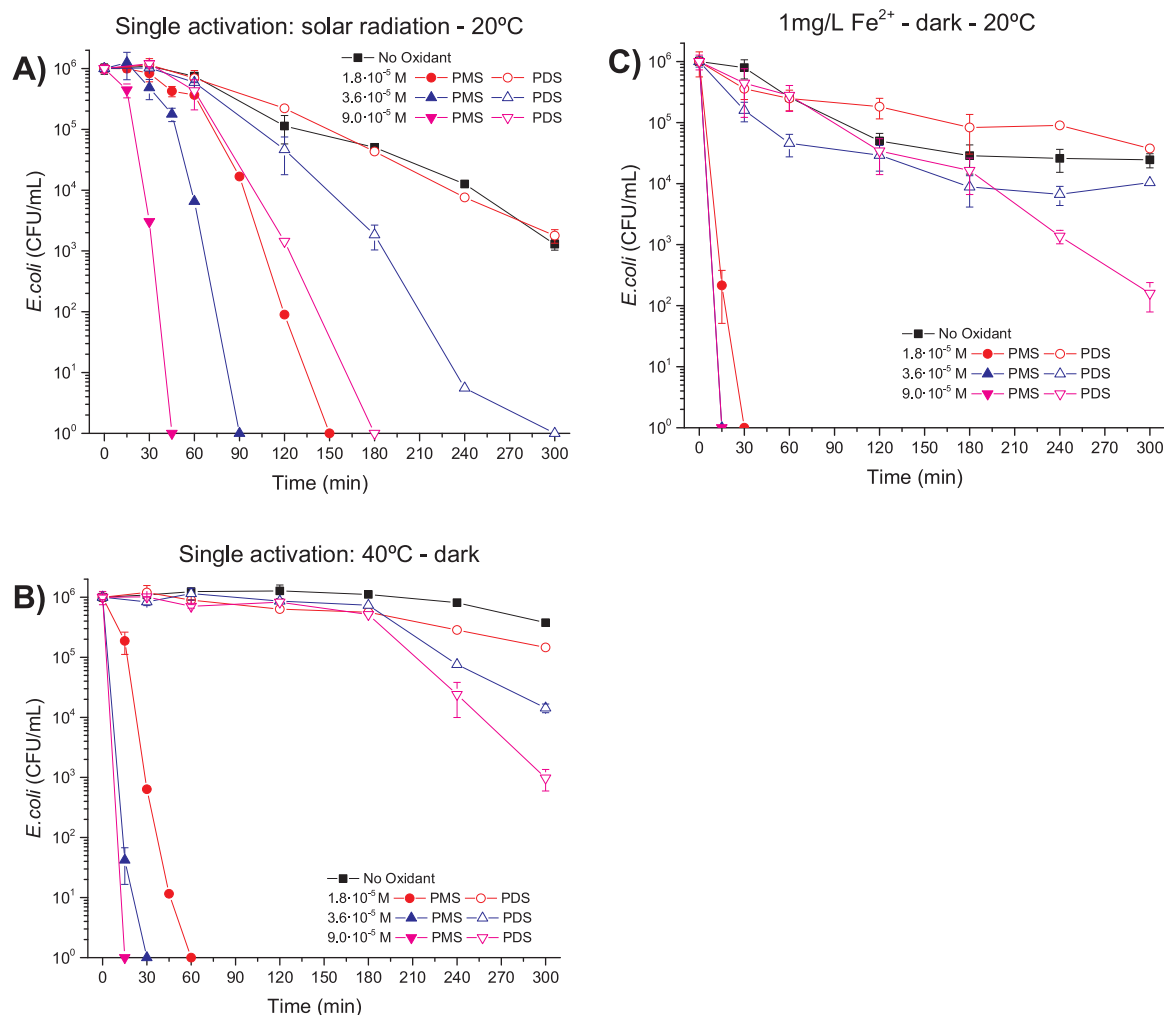


This catalytic cycle explains the dramatic difference between PDS/ $\text{Fe}(\text{II})$  and highly reactive PMS/ $\text{Fe}(\text{II})$ . Nevertheless, it should be considered that it was previously suggested [51] that the use of a higher PDS/ $\text{Fe}$  ratio than ours, because of the potential of iron species to act as scavengers, hence the low effectiveness for PDS.

#### 3.3. Double factor activation of PMS vs. PDS

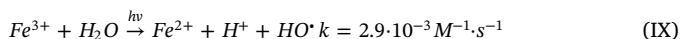
After the assessment of activation by individual factors (sunlight irradiation,  $\text{Fe}^{2+}$  or heat), the coupling of two factors to activate PDS and PMS was explored. The systems were: i)  $\text{Fe}^{2+}$ /40 °C (Fig. 2A); ii)  $\text{Fe}^{2+}$ /Sunlight at 20 °C (Fig. 2B); and iii) Sunlight at 40 °C (Fig. 2C). Also, the 1:5  $\text{Fe}^{2+}$ :PMS ratio will no longer be evaluated in the mechanistic studies, having shown strong effectiveness without need of further sunlight or heat activation.

As the baseline event, in absence of oxidants, the coupled systems  $\text{Fe}^{2+}$ /sunlight and sunlight/40 °C presented the faster inactivation rates, while poor performance is obtained with  $\text{Fe}^{2+}$ /40 °C. So, the key is the presence of  $\text{Fe}^{2+}$  and sunlight radiation (Fig. 2A–C). This combination can promote the generation of hydroxyl radicals as consequence of an intra-cellular photo-Fenton reaction [52,53], along with the external actions of  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$ . In presence of PMS or PDS, the coupled systems with PMS reached the highest efficiency in all the cases (total inactivation in less than 15 min with  $3.6 \cdot 10^{-5}$  M of PMS). The comparison with Fig. 1 shows clearly that double PMS activation is not favored, as it brings small improvement in inactivation times. The



**Fig. 1.** Single factor PMS and PDS activation. (a) simulated solar light activation at 900 W/m<sup>2</sup>, 20 °C and no iron. (b) iron activation at 1 ppm = 1.8·10<sup>-5</sup> M of Fe<sup>2+</sup>, 20 °C in the dark. (c) is thermal activation at 40 °C in dark and without iron.

presence of Fe<sup>2+</sup> as activator of PMS is determining in the inactivation rate as observed in equations VI and VII. However, this role of Fe<sup>2+</sup> for activating PDS is only relevant in presence of sunlight radiation. Fe<sup>3+</sup> participates in a regenerative catalytic cycle; under light, the process is photo-catalytic, due to the light-induced reduction of Fe<sup>3+</sup> back to Fe<sup>2+</sup>, due to the following Eq. IX [12].



This light-induced reduction of Fe<sup>3+</sup> generates hydroxyl radicals and Fe<sup>2+</sup> again available to react with PDS (Eq. 8). To summarize, according to Fig. 2, the best combination of PDS activation factors corresponds to the systems:

PDS/Fe(II)/Sunlight > PDS/Sunlight/40 °C > > PDS/Fe(II)/40 °C.

### 3.4. Triple activation of PMS and PDS

Fig. 3 shows that the triple activation of PMS (sunlight/Fe<sup>2+</sup>/40 °C) exhibits a similar bacterial decay to single Fe<sup>2+</sup> activation. This could be explained by the self-inhibition reactions that occur; Fe<sup>2+</sup> activation of PMS is highly efficient, and the presence of other activation factors maybe deprive the amount of Fe<sup>2+</sup> available to activate PMS, by the photo-oxidation and faster hydrolysis of Fe<sup>2+</sup>, that leads to Fe<sup>3+</sup>, while the regeneration cycling is somewhat slower.

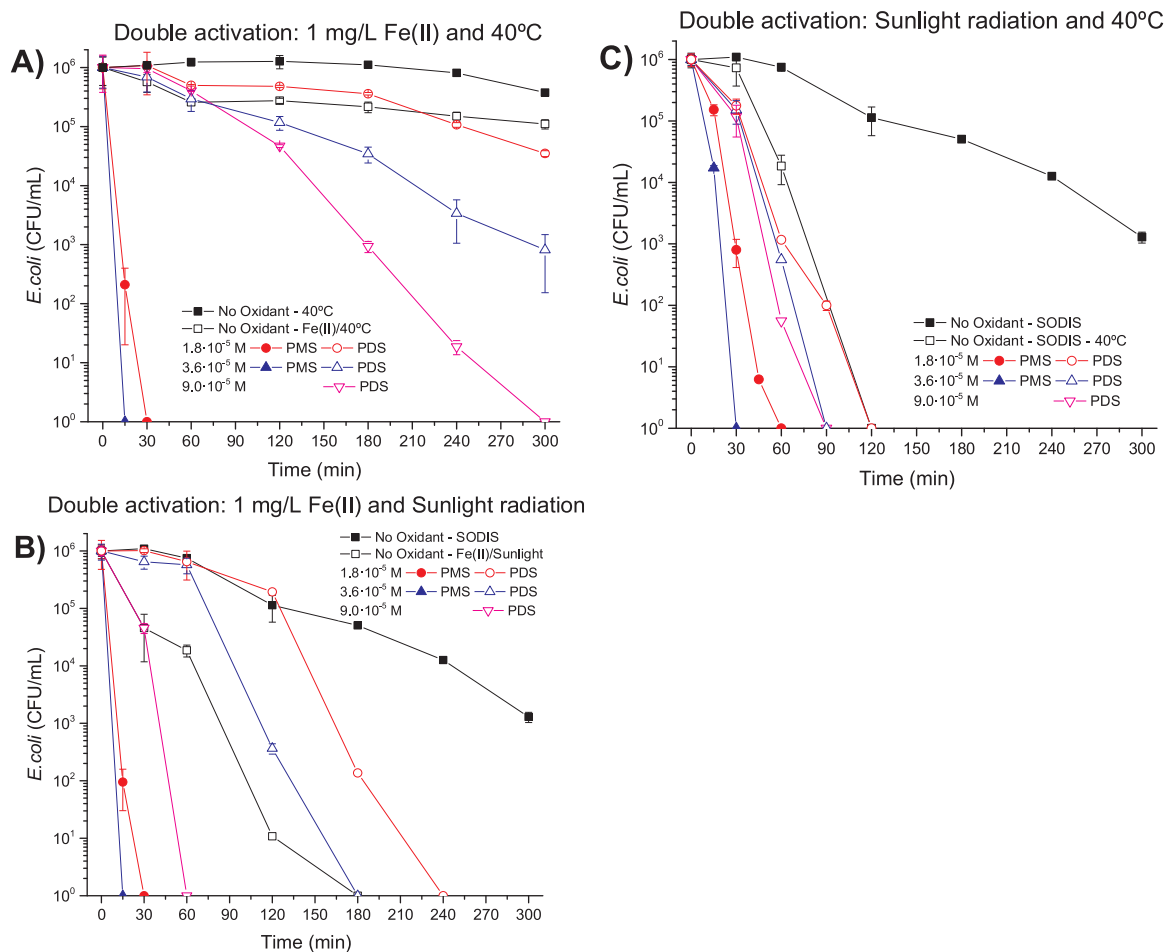
Neither in the case of PDS the triple activation shows an obvious

enhancement on bacterial decay. Indeed, with 1.8·10<sup>-5</sup> M of PDS, 120 min were required to get a bacterial reduction of 4-logU (Fig. 3), while total inactivation was reached in the same time with sole SODIS at 40 °C and only PDS/sunlight at 40 °C (Fig. 2C). A Fe<sup>2+</sup>/PDS ratio of 1:5 under sunlight at 40 °C shows an identical bactericidal efficiency with the double activation system PDS/Fe<sup>2+</sup>/sunlight, proving that heat at 40 °C is unnecessary when Fe<sup>2+</sup> and sunlight work as activators. This apparent “redundancy” is not actually a negative feature when the field application is considered. The results here show that this process is potentially not bound to thermal inactivation and could work in a larger range of seasons (colder weather) or be less affected by cloud/light intermittence.

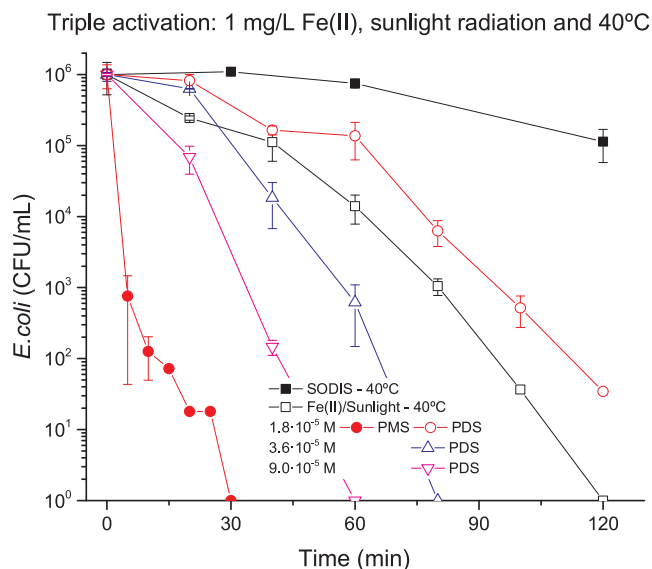
### 3.5. Comparison of mild PMS and PDS activation to micropollutants removal

The efficiency of the PMS and PDS-mediated treatment was assessed on the removal of a mixture of 13 different micropollutants (MPs, Table S1, Supplementary Material). The treatment processes were carried out using the best working conditions previously found for bacteria. Additional experiments were performed in water containing natural organic matter (NOM), to simulate the competition at the nm level taking place among MPs and NOM (Suwanee River NOM, SR NOM), and natural mineral iron as a substitute for Fe<sup>2+</sup> salts (Fig. 4 A–C).

As observed in the Fig. 4A, the combined process (CP) using PMS/Fe<sup>2+</sup>/sunlight (molar ratio 1:2) at 40 °C reached the highest



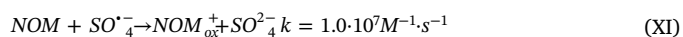
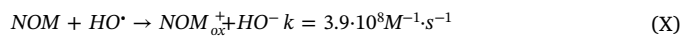
**Fig. 2.** Double factor PMS and PDS activation. (a) thermal activation at 40 °C in dark and 1 ppm =  $1.8 \cdot 10^{-5}$  M of  $\text{Fe}^{2+}$ . (b) simulated solar light activation at 900 W/m<sup>2</sup>, 40 °C and no iron. (c) simulated solar light activation at 900 W/m<sup>2</sup>, 20 °C and 1 ppm =  $1.8 \cdot 10^{-5}$  M of  $\text{Fe}^{2+}$ .



**Fig. 3.** Triple factor PMS and PDS activation: simulated solar light activation at 900 W/m<sup>2</sup>, 40 °C and 1 ppm =  $1.8 \cdot 10^{-5}$  M of  $\text{Fe}^{2+}$ .

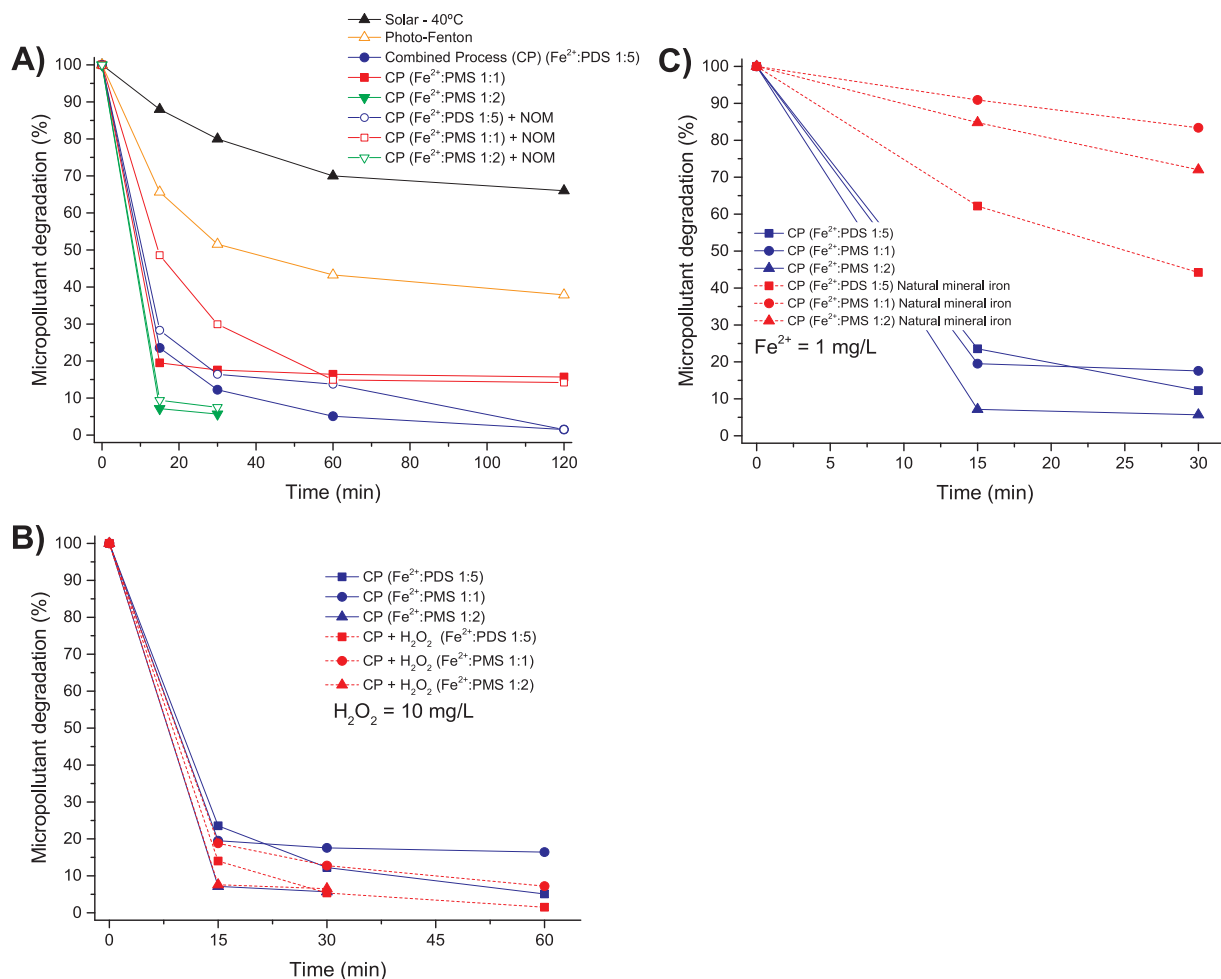
micropollutants abatement (95% in 15 min), while 60 min are required with PDS (molar ratio 1:5). In both cases, the efficiency is higher than photo-Fenton reaction and SODIS/40 °C. But, when the treatments are applied in presence of SR NOM the efficiency decreased, because of the

competition for generated free radicals. Nevertheless, the process is not hindered/blocked, especially in the case of PMS: $\text{Fe}^{2+}$  (ratio 1:1). NOM reacts with hydroxyl and sulfate radicals according to the following equations (Eqs. X and XI) [54]. The comparison of the reaction kinetics suggests that NOM is a more important sink for hydroxyl rather than sulfate radicals, as previously suggested; our results corroborate this fact and we postulate that this allows the decontamination process to effectively proceed (and in a similar case the bacterial disinfection), holding positive implications in the use of PMS/PDS in surface water treatment.



Although the MPs abatement can be slightly increased by addition of 10 mg/L of  $\text{H}_2\text{O}_2$ , reaching almost 90% of abatement with PDS (Fig. 4B), the efficiency decreased when natural mineral iron was used as activator (Fig. 4C), which is normal considering the heterogeneous activation of PMS and PDS. Under these conditions, the highest abatement is reached with 1:5 PDS ratio (55%, 30 min). This is particularly interesting concerning the degradation mechanism. PDS produces two sulfate radicals while PMS a sulfate and a hydroxyl radical. Although in bacterial inactivation the non-selectivity and the rapid reaction of  $\text{HO}^\bullet$  is desired, when it comes to micropollutants, the longer lifetime and higher selectivity of  $\text{SO}_4^{\bullet-}$  will confer significant changes in the degradation pathway. We suggest that the  $\text{HO}^\bullet$  will be more easily consumed in the degradation of the intermediates of the organic contaminants, while  $\text{SO}_4^{\bullet-}$  will selectively oxidize the parent





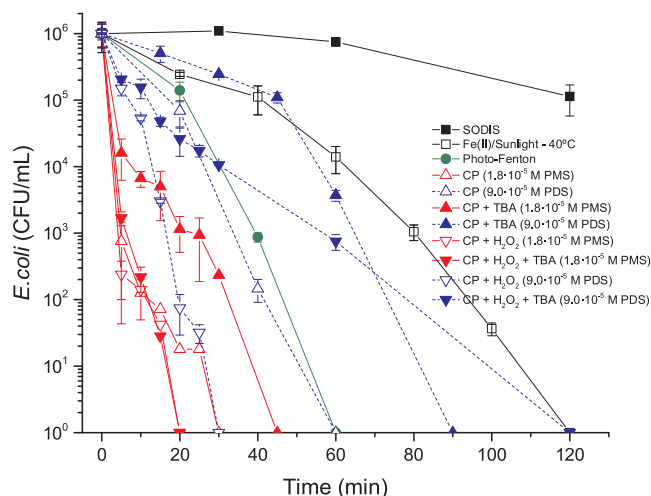
**Fig. 4.** Micropollutants removal: (a) comparison of combined process (CP, triple activation) with photo-Fenton and influence of Natural Organic Matter (2 mg TOC/L SR NOM); (b) comparison of combined processes with addition of  $2.9 \cdot 10^{-4}$  M H<sub>2</sub>O<sub>2</sub>; (c) comparison of combined process with addition of Fe<sup>2+</sup> or 2 ppm of natural iron.

compounds. This would cause their apparent elimination, or better put, the disappearance of the parent compounds from the LC/MS method used to quantify MPs in water. Some authors have reported the great efficiency of PMS and PDS activation in the removal of different organic micropollutants [24,25,31,55,56], however, there are no references in the context of SODIS. The comparison with bacteria allows to hold promise on the disinfection/decontamination in different SODIS contexts, with natural Fe present, even without H<sub>2</sub>O<sub>2</sub>.

### 3.6. PMS and PDS multi-activation in presence of H<sub>2</sub>O<sub>2</sub>

When H<sub>2</sub>O<sub>2</sub> was added to the PMS and PDS activated by light and Fe<sup>2+</sup> at 40 °C, an enhancement was previously observed. Further investigating the process, we can consider that a photo-Fenton is generated in parallel, which will enhance the overall bactericidal process. The experiments presented in Fig. 5 used a 1:10 ratio of Fe<sup>2+</sup>:H<sub>2</sub>O<sub>2</sub> (in mg/L). In addition, the efficiency of bacterial decay in presence of tert-butanol (TBA) as hydroxyl and sulfate radical scavenger was tested [57], in order to elucidate the complex inactivation mechanism.

As observed in the Fig. 5, we found that 60 min are necessary to reach total bacterial inactivation using photo-Fenton process, while only 30 min were required with PMS triple activation (CP). The combination of PMS and H<sub>2</sub>O<sub>2</sub> significantly enhanced the disinfecting rate of photo-Fenton, reaching the total inactivation at 20 min. On the other hand, TBA produced a clear reduction of the bacteria inactivation kinetics due to its role of scavenger towards hydroxyl and sulfate radicals,



**Fig. 5.** Triple activation of PMS and PDS and radical scavenging experiments. All reactions are performed at 40 °C under simulated solar light (900 W/m<sup>2</sup>) with 1 ppm Fe<sup>2+</sup> (except SODIS). SODIS process corresponds to simulated solar light at 900 W/m<sup>2</sup> at 20 °C.  $1.8 \cdot 10^{-5}$  M of PMS or  $9 \cdot 10^{-5}$  M of PDS are added for CP, PF with PMS or PDS, CP + TBA and PF with PDS + TBA. Reactions with hydrogen peroxide (PF) are adjusted to  $2.9 \cdot 10^{-4}$  M H<sub>2</sub>O<sub>2</sub> (corresponding to a 1:10 Fe<sup>2+</sup> to H<sub>2</sub>O<sub>2</sub> ratio). TBA concentration is of 0.1 M when present.

except in the combination of PMS and  $\text{H}_2\text{O}_2$ . This effect could be explained by the 1000-fold higher reactivity of Fe with PMS than with  $\text{H}_2\text{O}_2$ , making this reaction the main inactivation pathway, hence the high sulfate radical production still is inactivating bacteria (see supplementary Table S2 for the kinetic constants). Another hypothesis could be related with the large generation of hydroxyl and sulfate radicals and the short time of reaction, making TBA unable to scavenge all generated radicals.

In the case of PDS, the efficiency of its triple activation is the same as with the photo-Fenton reaction (Fig. 5). However, this efficiency was significantly enhanced by combination of photo-Fenton and PDS, reducing the reaction time by half. On the other hand, the addition of TBA to triple activated PDS increased the time necessary to reach total disinfection from 60 min to 90 min. These results suggest the latter presence of hydroxyl radicals in the activation of PDS, which could be formed according to Eqs. III and IV. When TBA is added to photo-Fenton/PDS system, the time for total inactivation was increased from 30 to 120 min. Most likely, the presence of both PDS and  $\text{H}_2\text{O}_2$  and the 3-fold faster reaction between the latter and iron makes the  $\text{HO}^\bullet$  pathway prevalent and gets scavenged by TBA effectively. Also, the same reaction oxidizes  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  which reduces the availability of  $\text{Fe}^{2+}$  to react with PDS. Since the catalytic regeneration shown in PMS does not take place, the delay is a normal consequence. However, these results were still faster than the ones obtained without PDS, confirming the participation of sulfate radicals in the disinfection process and confirm the presence of hydroxyl radicals as well. Finally, it is asserted here that in a complex system, PMS is the preferred oxidant.

### 3.7. Comparison of PMS, PDS and photo-Fenton processes for the disinfection of natural surface (lake) water

In order to assess primarily the feasibility of this process in disinfecting natural water, where the presence of ions and NOM is expected to hinder the radicals' action, we present Fig. 6 which shows *E. coli* decay by light-activated PMS and PDS at 20 and 40 °C (Fig. 6A and B), to dissociate the blank runs and temperature effects. As expected, the temperature favors the rise of disinfection rate via the thermal activation of PMS and PDS. The higher activity of PMS is demonstrated in a real water matrix at 40 °C as 5-fold lower concentration than PDS. Both, PMS and PDS, are considerably better activated by temperature than  $\text{H}_2\text{O}_2$ .

Fig. 7 shows the disinfection efficiency by the combined processes with PMS or PDS at 40 °C. Under these conditions, total *E. coli* inactivation was reached after 45 and 60 min  $3.6 \cdot 10^{-5}$  and  $1.8 \cdot 10^{-5}$  M of PMS respectively. While  $3.6 \cdot 10^{-5}$  M of PDS needed 90 min. Also, another important point to note is the correlation of lake water results with Milli-Q water in the first part of the manuscript. The comparison of Figs. 5 and 8 shows that treatments over lake water are slower. The lake water matrix contains organic matter and other ions that compete with the process (as shown before for NOM) or the ions presence might exhibit a scavenging effect. Nevertheless, an increase of PMS concentration is sufficient to achieve lake water disinfection with the same efficiency as in Milli-Q. In any case, the amount of PMS needed to reach total inactivation of lake water is sufficiently little to assume a low impact in the final economical cost or possibly in human health. Furthermore, both water samples present pH differences. While Milli-Q water pH is around 6, the lake water is approximately 8.5. Taking into account that treatment was performed without pH modifications, these different pH levels imply differences in the efficiency of oxidants (mainly PMS and PDS) and the availability of dissolved iron in water, that favor photo-Fenton and Fe-mediated activation. Although the use of PMS is not highly pH-dependent [18], some authors have reported a higher activation of PMS and PDS over alkaline conditions [58,59] because of the decomposition of sulfate radicals to hydroxyl radicals. As such, the different pH of water samples tested has to be taken into account as a factor that could affect the disinfection efficiency.

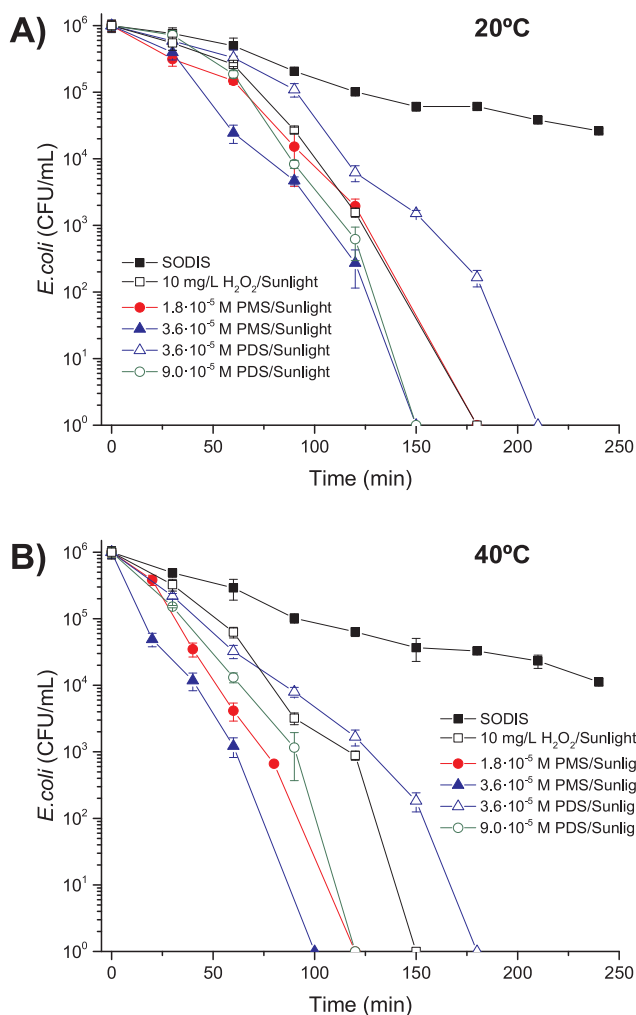


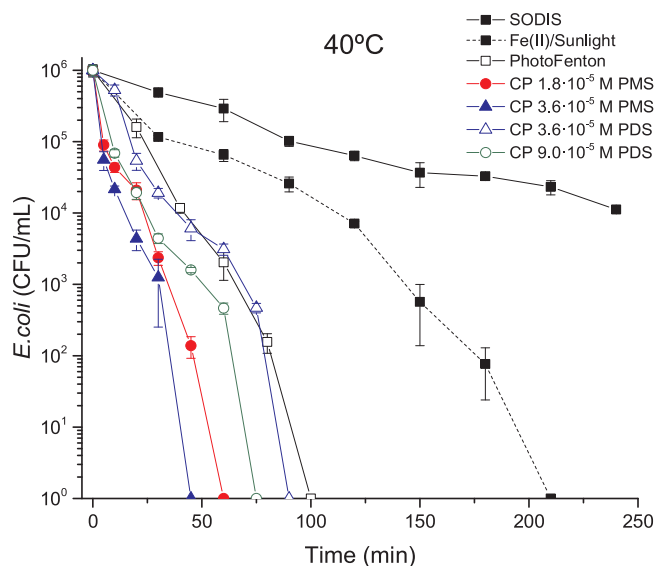
Fig. 6. Comparison of treatments over lake water samples. (a) single activation of PMS and PDS, simulated solar light ( $900 \text{ W/m}^2$ ) at 20 °C. (b) double activation, simulated solar light ( $900 \text{ W/m}^2$ ) at 40 °C. Photo-Fenton experiments are performed with  $2.9 \cdot 10^{-4} \text{ M H}_2\text{O}_2$  (corresponding to a 1:10  $\text{Fe}^{2+}$  to  $\text{H}_2\text{O}_2$  ratio).

Nevertheless, the results obtained with real lake water are of high importance, depicting close-to-field operating conditions, and a good correlation of the relative difference among the processes in controlled conditions (aseptic/sterile reactors, lab strain of *E. coli*, continuous light supply etc.), as well as its feasibility.

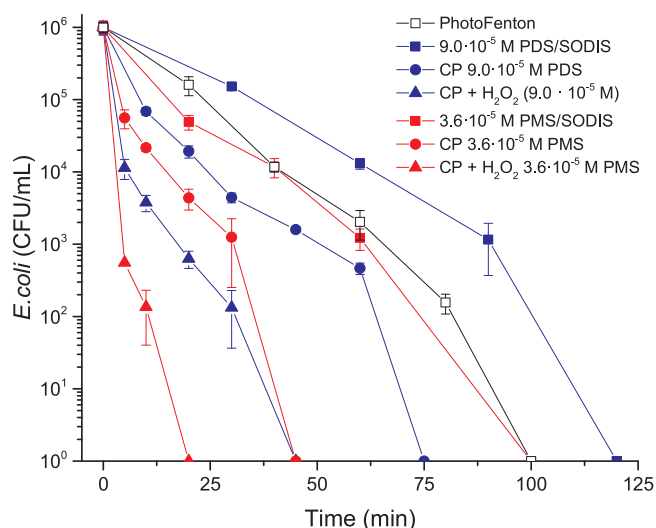
The reaction time can be reduced even more, if a fourth activator is introduced, in this case by combination of PMS or PDS with  $\text{H}_2\text{O}_2$ , keeping the previous conditions similar. As observed in Fig. 8, this combination of PMS or PDS with  $\text{H}_2\text{O}_2$  significantly reduced the reaction time required to reach total inactivation. For instance, in the case of PDS, the reaction time is reduced from 75 min required with the combined process to 40 min if  $\text{H}_2\text{O}_2$  is added. Again the best efficiency was reached through the use of  $3.6 \cdot 10^{-5} \text{ M PMS}$  and  $\text{H}_2\text{O}_2$ . Except for the case of PDS/SODIS, the rest of the treatments represented in Fig. 8 are more effective than photo-Fenton reaction. These results are promising from the point of view of real application for the improvement of SODIS treatments.

### 3.8. Integrated mechanistic proposition for the PMS or PDS activation and subsequent oxidative species generation that lead to bacterial inactivation

Based on the relevant literature and the experiments conducted in this work, we have synthesized and hereby propose an integrated



**Fig. 7.** Comparison of triple activation treatments over lake water samples. Simulated solar light ( $900 \text{ W/m}^2$ ),  $1 \text{ ppm} = 1.8 \cdot 10^{-5} \text{ M}$  of  $\text{Fe}^{2+}$  and  $40^\circ\text{C}$ . PhotoFenton are adjusted to  $2.9 \cdot 10^{-4} \text{ M}$   $\text{H}_2\text{O}_2$  (corresponding to a 1:10  $\text{Fe}^{2+}$  to  $\text{H}_2\text{O}_2$  ratio).



**Fig. 8.** Comparison of double and triple activation of PMS and PDS with photo-Fenton with PMS or PDS in lake water samples.  $3.6 \cdot 10^{-5} \text{ M}$  of PMS or  $9 \cdot 10^{-5} \text{ M}$  of PDS are added for double and triple activation (CP) and photo-Fenton with PMS or PDS. PhotoFenton experiments are adjusted to  $2.9 \cdot 10^{-4} \text{ M}$   $\text{H}_2\text{O}_2$  (corresponding to a 1:10  $\text{Fe}^{2+}$  to  $\text{H}_2\text{O}_2$  ratio).

mechanism for the inactivation of *E. coli* by means of PMS or PDS as oxidant. In Fig. 9, we account for the heat, Fe or solar-mediated PMS/PDS activation, presenting a scheme combining all the possible combinations, initiated by either of the two precursors. Special emphasis has been given on the initial reactant and the final product, which has proven or postulated bactericidal efficiency. A summary of the radical generation, propagation and termination reactions is given in Table S2 (Supplementary material).

Initially, PMS/PDS generate oxidative species by any number of present activation factors, namely Fe, mild heat and/or UVA. According to the added oxidant, the result differs immediately by generation of  $\text{SO}_4^{\cdot-}$  and/or  $\text{HO}^\bullet$ . If  $\text{Fe}^{3+}$  is present, there is an efficient catalytic cycle taking place by either the solar-assisted reduction of ferric species in water or their reaction with PMS, leading to  $\text{Fe}^{2+}$  and  $\text{SO}_5^{\cdot-}$ . Ferrous iron re-participates in activation of PMS and generates further transient

species. However, if PDS is used, only the solar-mediated reduction takes place and is therefore slower, as already found from our results; PMS even in the dark can maintain an auto-catalytic cycle.

Following, the reactions that ensue are many orders of magnitude faster, and involve radical transformation/reaction pathways. It is important to highlight the interchangeability among the sulfate and hydroxyl radicals, as well as the generation of  $\text{SO}_5^{\cdot-}$ , which is oxidative and most probably fatal for bacteria, regardless of the starting oxidant. This indicates that at a second level, both processes are generating  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^\bullet$ , but at rate controlled steps, and their recombination (especially  $\text{SO}_5^{\cdot-}$ ) regenerates the initial PMS/PDS addition. Also, this indicates that since  $\text{HO}^\bullet$  are produced in both reactions, its recombination will generate  $\text{H}_2\text{O}_2$ .

The generation of  $\text{H}_2\text{O}_2$  is a very critical step in the reaction pathway. Its presence will fuel a Fenton process with the ferrous iron added in the bulk. The Fenton process is responsible for further radical production even without the addition of  $\text{H}_2\text{O}_2$ . However, this is not the most important implication taking place, as the presence of  $\text{H}_2\text{O}_2$  and the reduction of  $\text{Fe}^{3+}$  species, or the reaction with  $\text{HO}^\bullet$ , leads to  $\text{HO}_2^\bullet$ , which has a high significance either as an oxidative species (attacking bacteria) or as a ferric species-reducing compound. The catalytic regeneration of ferric to ferrous species can lead to further activation of PMS/PDS or Fenton process. Also, there are less efficient processes taking place, transformation among radicals and generation of lower oxidative ones, or replenishment of  $\text{H}_2\text{O}_2$  amounts. Finally, the cycle of reaction closes with the recombination and return to non-excited states for  $\text{SO}_4^{\cdot-}$ ,  $\text{SO}_5^{\cdot-}$ ,  $\text{HO}_2^\bullet$  and  $\text{HO}^\bullet$  radicals.

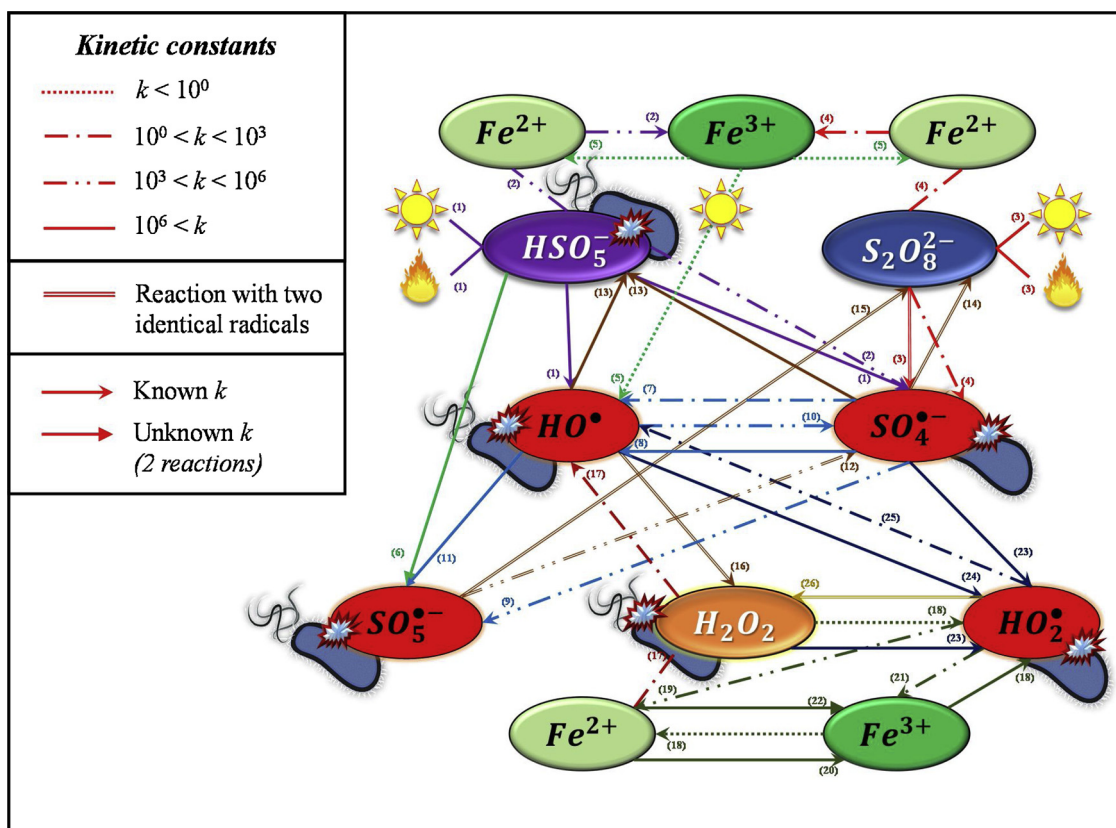
### 3.9. Economic analysis: Normalization of disinfection efficiency by unit cost

The results presented so far prove the existence of different agents able to reduce significantly the contact time required to reach total inactivation of *E. coli* without a high increase of cost treatment, since some of these parameters already occur in SODIS treatment, as for example (mild) heating. Normally, water exposure to solar radiation reaches temperatures higher than  $30$  and  $40^\circ\text{C}$  in CPC reactors and PET bottles respectively, while solar radiation does not infer an economical cost; only the addition of reagents such as PDS, PMS and  $\text{H}_2\text{O}_2$  would increase the operational cost of the treatment. Therefore, by the addition of low concentrations of PMS/PDS, SODIS treatment could be considerably enhanced, because iron is ubiquitous in natural waters in SODIS-candidate areas, and even in cloudy days, just the combination PMS/ $\text{Fe}^{2+}$  with the mild ambient temperature is able to reach a significant level of inactivation. However, before generalizing to the field applications, a small-scale economical investigation is in order.

Table 1 shows the operational conditions of the used treatment methods economically assessed, the prices of the required reagents in €/mol. In addition, this Table shows the costs of water considering the enhanced SODIS treatments in the standard 2-L PET bottle. An estimation of the yearly cost (€/m<sup>3</sup>) for a family of 4 members is also presented. Here, a consumption of water in sub-Saharan countries is presumed around 25 L per person and day. However, this value is susceptible of variations depending on the regions, normally being smaller in areas of hydric stress. Considering these values, the water consumption of an African family would be around 36,500 L/year. Considering the above and the results already presented, Fig. 10 compares the cost of the enhanced SODIS processes and the time required to obtain the total inactivation of *E. coli*.

As observed, the lower reaction time needed, the higher operational cost; the cheapest one corresponds to SODIS treatment, because it does not involve cost of reagents. Therefore, only considering the treatments using chemical reagents, SODIS/ $\text{Fe}^{2+}$  would be the cheapest treatment (0.0024 €/family·year). Even SODIS/ $\text{Fe}^{2+}$ , could be even considered as null, due to natural mineral iron present in water could substitute commercial  $\text{Fe}^{2+}$  with similar efficiencies. This consideration could be also taken into account for the rest of iron mediated treatments. The





**Fig. 9.** Overall mechanistic proposal for the three-factor activation of PMS/PDS, and the subsequent bacterial disinfection. White fonts indicate the more stable species (PMS, PDS,  $H_2O_2$ ) and black fonts the rest; red circles signify the radical species and green the iron ions. Please note the colors' correspondence of the lines and reaction numbers with the reactions presented in Table S2 (Supplementary Material) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

cost increased when oxidants were added. Although there are not high differences between the different oxidation treatments, the higher cost of PMS rises the price of these treatments. The highest price corresponds to CP +  $H_2O_2$  (with PMS). This treatment reached total inactivation of *E. coli* after 20 min, and it adds up to a cost of 1.94 €/family-year. The cost is considerably lower if PMS is changed by PDS, in this case the cost is 0.94 €/family-year, but the time to reach the total inactivation is more than double (45 min).

These low operational costs reinforce the arguments to use AOPs in the enhancement of SODIS. We show that it is possible to obtain safe water reducing the time required for SODIS treatment with an acceptable cost for African families, living with less than 50 €/month. It is important to remark, that the United Nations General Assembly [60]

approved that the cost of water should not exceed 3% of household income. In addition, these operational costs are calculated for treatment in 2 L PET bottles, but of course the operational cost could be decreased by using a bigger facility, for example a CPC reactor, able to treat more water in less time than SODIS treatment. The implications of the results and the view of the economical estimates are higher for countries with higher needs of water, more availability of means but still with contaminated sources. Higher amounts of water can be treated without the bottlenecks of the traditional SODIS process.

Concerning the consumer safety of the process, without researching the toxicity of residual oxidants, definite conclusions cannot be drawn. However, an estimation of the dangers can be suggested. PDS and PMS are classified as a corrosive and an oxidizing agent respectively, and

**Table 1**

Operating conditions considered for economic analysis enhanced SODIS treatments and prices estimated to treat: 2 L of water (2 L PET bottle); 1 m<sup>3</sup>; and 36.5 m<sup>3</sup> (estimated consumption of water per year for a family of 4 members).

Reagent	[PMS] M	[PDS] M	[H <sub>2</sub> O <sub>2</sub> ] M	[Fe(II)] M	Time for total inactivation (min)	Treatment cost (€) (2 L PET bottle)	€/m <sup>3</sup>	Treatment cost per year (€) (4 members family)
**Price (€/mol)	1.1408	0.151	0.0419	0.0036				
Treatment								
SODIS					> 300	0	0	0
SODIS/Fe(II)				0.000018	210	1.30104·10 <sup>-7</sup>	6.5052·10 <sup>-5</sup>	0.0024
H <sub>2</sub> O <sub>2</sub> /SODIS			0.00029		150	2.43258·10 <sup>-5</sup>	0.0122	0.4439
PDS/SODIS		0.00009			120	2.71778·10 <sup>-5</sup>	0.0136	0.4960
PMS/SODIS	0.000036				100	8.21373·10 <sup>-5</sup>	0.0411	1.4990
Photo-Fenton			0.00029	0.000018	100	2.44559·10 <sup>-5</sup>	0.0122	0.4463
CP with PDS		0.00009		0.000018	75	2.73079·10 <sup>-5</sup>	0.0136	0.4984
CP with PMS	0.000036			0.000018	45	8.22674·10 <sup>-5</sup>	0.0411	1.5014
CP with PDS + H <sub>2</sub> O <sub>2</sub>		0.00009	0.00029	0.000018	45	5.16337·10 <sup>-5</sup>	0.0258	0.9423
CP with PMS + H <sub>2</sub> O <sub>2</sub>	0.000036		0.00029	0.000018	20	1.06593·10 <sup>-4</sup>	0.0533	1.9453

\*\* [61].

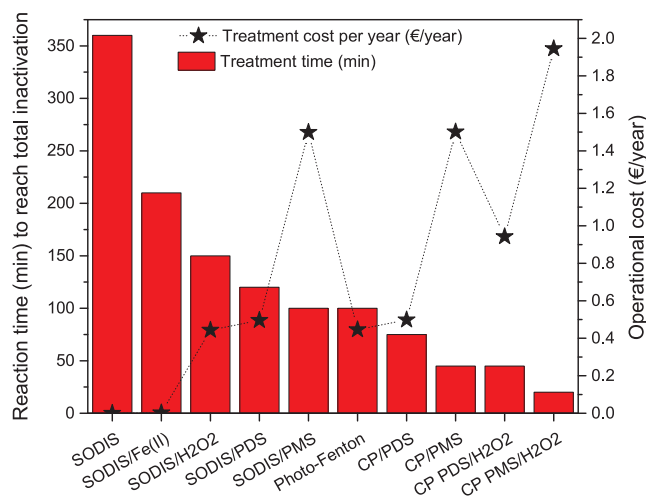


Fig. 10. Economical cost (€/cell) comparison of each treatment to disinfect lake water. SODIS is not included (no cost).

according to German Water Hazard Class (WGK) they have low hazard to waters (level 1 out of 3). Hence, their use is not prohibited by default, but a systematic assessment of the acute toxic effects prior to treatment would be imperative in the future.

#### 4. Conclusions

This manuscript reports for the first time the disinfection efficiency of enhanced SODIS treatment in mild conditions by addition of PMS or PDS as precursors of sulfate and/or hydroxyl radicals. Because of the low efficiency of PMS and PDS by themselves, the use of activation agents to reduce the reaction time to inactivate *E. coli* is recommended. For that, in a first approach PMS and PDS activation is evaluated using different activation factors, such as  $\text{Fe}^{2+}$ , sunlight and heating. The highest efficiencies were obtained in a combined process using the three activation factors.

PMS always showed a higher efficiency than PDS, mainly because of the generation of sulfate and hydroxyl radicals at the same time. Besides, the combination of PMS and  $\text{Fe}^{2+}$  drastically decreased bacterial concentration. When  $\text{Fe}^{2+}$  is oxidized to  $\text{Fe}^{3+}$ , there is an efficient catalytic cycle taking place by either the solar-assisted reduction of ferric species in water or their reaction with PMS. This catalytic cycle explained the dramatic difference in the case of coupling PDS/ $\text{Fe}^{2+}$ , with poorer results when compared to PMS/ $\text{Fe}^{2+}$ . In addition, the combined process with PMS or PDS reached a faster bacterial inactivation than a well-established AOP, the photo-Fenton process. With all the information, the integrated mechanistic for the activation of PMS and PDS is proposed, showing the different oxidative species acting in the inactivation of bacterial inactivation. Besides, this work demonstrated the efficiency of SR-AOPs not only to inactivate pathogen germs as *E. coli*, but also to remove organic micropollutants of emerging concern. The same operating conditions applied for disinfection (low concentrations of PMS and PDS) are able to remove a mixture of 13 micropollutants ( $\mu\text{g/L}$ ) at a rate of more than 90% in 15 min.

The economic analysis proved that these treatments are feasible to apply in developing countries without access to safe water, and with low incomes. The most expensive scenario coincides with the most effective one (total inactivation of *E. coli* after 20 min with the Combined Process using PMS and  $\text{H}_2\text{O}_2$ , with a cost of 1.94 €/family-year. In general terms, because of the independence of SODIS from electricity that would be required to irradiate and to heat water, the above-mentioned processes are very cheap and feasible treatment methods in developing countries without the facilities required to supply safe drinking water.

The cost could be reduced with the use of higher facilities, for instance low-cost compound parabolic collector (CPC) reactors able to treat higher volumes of water per surface. However, this economical assessment does not take into account non-experimental associated costs, such as the cost of reagent's transport until the point of use, and the costs related with importing/exporting, contracts as a function of safety etc. The need to safety transport these substances, for people and environment, could rise largely the prices, and for that it is important to keep this factor in mind before a final decision can be made.

#### Acknowledgements

The authors would like to thank the Swiss National Foundation for the "SNF Scientific Exchanges" Grant (No. 180499) for the research stay of Jorge Rodríguez-Chueca at École Polytechnique Fédérale de Lausanne. The authors would also like to acknowledge the European project WATERSPOUTT H2020-Water-5c-2015 (GA 688928) and the Swiss State Secretariat for Education, Research and Innovation for the financial support (SEFRI-WATERSPOUTT, No. 588141). Besides, Jorge Rodríguez-Chueca acknowledges Universidad Politécnica de Madrid for the project VJIDOCUPM18JJRC.

#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.02.018>.

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